



# PORE STRUCTURE OF CEMENT-BASED MATERIALS

TESTING, INTERPRETATION AND REQUIREMENTS

KALLIOPI K. ALIGIZAKI

# Contents

<i>List of figures</i>	xiii
<i>List of tables</i>	xix
<i>Foreword</i>	xxi
<i>Preface</i>	xxiii
<i>Acknowledgments</i>	xxv
<i>List of symbols</i>	xxvii
<i>List of abbreviations</i>	xxxv
<i>Units and conversions</i>	xxxix

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	<i>Scope of the book</i>	3
1.2	<i>Pores in cement paste</i>	4
1.2.1	Gel pores	5
1.2.2	Capillary pores	9
1.2.3	Hollow-shell pores	10
1.2.4	Air voids	11
1.2.5	Pore size ranges	11
1.3	<i>Methods for characterizing pore structure</i>	14
1.4	<i>Definition of pore structure parameters</i>	16
1.4.1	General pores	16
1.4.1.1	<i>Porosity</i>	17
1.4.1.2	<i>Hydraulic radius</i>	17
1.4.1.3	<i>Specific surface area</i>	18
1.4.1.4	<i>Threshold diameter</i>	19
1.4.1.5	<i>Pore size distribution</i>	20
1.4.1.6	<i>Other parameters</i>	21
1.4.1.7	<i>Factors affecting the parameters measured</i>	26
1.4.2	Air voids	27
1.4.2.1	<i>Total air content</i>	27
1.4.2.2	<i>Specific surface</i>	27
1.4.2.3	<i>Spacing factor</i>	28
	<i>References</i>	30

2 Specimen pretreatment	34
2.1 Water removal 34	
2.1.1 Drying techniques 35	
2.1.1.1 <i>Oven-drying</i> 35	
2.1.1.2 <i>Vacuum-drying</i> 36	
2.1.1.3 <i>P-drying</i> 36	
2.1.1.4 <i>D-drying</i> 36	
2.1.1.5 <i>Direct freeze-drying</i> 37	
2.1.1.6 <i>Indirect freeze-drying</i> 38	
2.1.1.7 <i>Desiccant drying</i> 38	
2.1.1.8 <i>Critical point drying</i> 38	
2.1.2 Solvent replacement 41	
2.1.2.1 <i>Ease of penetration</i> 43	
2.1.2.2 <i>Physical and chemical interactions</i> 44	
2.1.3 Comparison of different water removal techniques 45	
2.2 Preparation for microscopy 47	
2.2.1 Polished surface 48	
2.2.1.1 <i>Cutting, grinding, and polishing</i> 48	
2.2.1.2 <i>Impregnation by epoxy resin</i> 49	
2.2.2 Thin sections 52	
2.2.3 Fracture surface 54	
2.2.4 Intrusion alloys 55	
References 57	
3 Mercury intrusion porosimetry 60	
3.1 Theory and testing procedure 61	
3.1.1 Instrument description 61	
3.1.2 Testing procedure 63	
3.1.2.1 <i>Low pressure</i> 63	
3.1.2.2 <i>High pressure</i> 64	
3.1.3 Calculation of pore size 65	
3.1.4 Pore size distribution 68	
3.1.5 Specific surface area 69	
3.2 Plots obtained 70	
3.2.1 Cumulative intrusion curves 72	
3.2.2 Incremental and differential distribution curve 75	
3.2.3 Surface area 77	
3.2.4 Range of sizes determined 77	
3.3 Hysteresis and entrapment of mercury 78	
3.3.1 Theories proposed to explain hysteresis 79	
3.3.1.1 <i>Ink-bottle pores and trapped mercury</i> 80	
3.3.1.2 <i>Contact angle hysteresis</i> 81	
3.3.1.3 <i>Pore potential theory</i> 82	

3.3.1.4	<i>Surface roughness</i>	83
3.3.1.5	<i>Compression of the solid</i>	83
3.3.2	Entrapment of mercury and second intrusion method	84
3.4	<i>Parameters affecting results</i>	86
3.4.1	Specimen pretreatment	86
3.4.2	Specimen size	89
3.4.3	Rate of pressure build-up	91
3.4.4	Contact angle	91
3.4.4.1	<i>Parameters affecting contact angle</i>	92
3.4.4.2	<i>Determination of contact angle</i>	94
3.4.5	Surface tension of mercury	96
3.4.6	Alteration of pore structure	97
3.4.6.1	<i>Reintrusion of mercury</i>	97
3.4.6.2	<i>Microscopic examination</i>	98
3.4.7	Alternative intrusion liquids	99
3.5	<i>Advantages and limitations</i>	100
	<i>References</i>	102
4	<b>Gas adsorption</b>	108
4.1	<i>Theory and testing procedure</i>	109
4.2	<i>Analysis of data</i>	112
4.2.1	Adsorption isotherm	112
4.2.2	Thickness of adsorbed film	116
4.2.3	Pore size (Kelvin equation)	120
4.3	<i>Total pore volume</i>	122
4.3.1	Dubinin–Radushkevich equation	123
4.4	<i>Pore size distribution</i>	124
4.4.1	The Barrett–Joyner–Halenda method	126
4.4.2	The Cranston–Inkley method	127
4.4.3	The modelless method and micropore (MP) analysis method	127
4.5	<i>Specific surface</i>	132
4.5.1	The Langmuir theory	133
4.5.2	The Brunauer–Emmett–Teller (BET) theory	134
4.5.3	The Dubinin–Kaganer equation	138
4.5.4	The Harkins–Jura (HJ) relative method	139
4.5.5	The <i>t</i> -plot	140
4.5.6	The $\alpha_s$ -plot	143
4.6	<i>Adsorption hysteresis</i>	146
4.7	<i>Factors affecting the results</i>	151
4.7.1	Pretreatment method	151
4.7.2	Type of adsorbate used	153
4.7.3	Analysis method used	157

4.8	<i>Advantages and limitations</i>	159
	<i>References</i>	162
5	<b>Pycnometry and thermoporometry</b>	168
5.1	<i>Pycnometry</i>	168
5.1.1	Liquid pycnometry	170
5.1.1.1	<i>Water absorption</i>	171
5.1.1.2	<i>Water replacement using an alcohol</i>	172
5.1.2	Gas (helium) pycnometry and helium flow	175
5.1.2.1	<i>Theoretical aspects</i>	176
5.1.2.2	<i>Helium flow</i>	178
5.1.2.3	<i>Determination of surface area and hydraulic radius</i>	182
5.1.2.4	<i>Effect of pretreatment</i>	183
5.1.3	Advantages and limitations	184
5.2	<i>Thermoporometry</i>	184
5.2.1	Theoretical considerations	185
5.2.2	Experimental procedure	187
5.2.3	Pore size distribution	190
5.2.4	Determination of the surface area and the average radius	191
5.2.5	Applications on cement paste	191
5.2.6	Advantages and limitations	192
	<i>References</i>	192
6	<b>Nuclear magnetic resonance</b>	196
6.1	<i>Theoretical aspects/fundamentals</i>	197
6.1.1	Single nucleus properties	197
6.1.2	Magnetization of a group of nuclei (bulk magnetization)	201
6.2	<i>NMR experiment</i>	205
6.2.1	Instrumentation	205
6.2.2	NMR excitation and response	208
6.2.2.1	<i>Free induction decay</i>	208
6.2.2.2	<i>Fourier transformation and spectrum</i>	210
6.2.3	Pulse sequences	211
6.2.3.1	<i>Hahn spin echo pulse sequence</i>	211
6.2.3.2	<i>Inversion recovery pulse sequence</i>	212
6.2.3.3	<i>Carr-Purcell echo pulse sequence</i>	213
6.3	<i>Spin relaxation</i>	214
6.3.1	Spin-lattice relaxation	216
6.3.2	Spin-spin relaxation	217
6.3.3	Inhomogeneous broadening	217

6.4	Pore size determination	219
6.4.1	Magnetic-resonance relaxation analysis	220
6.4.1.1	Relaxation inside a single pore	224
6.4.1.2	Relaxation inside a distribution of pore sizes	226
6.4.1.3	Pore size distribution in cement pastes	229
6.4.2	NMR cryoporometry	232
6.4.3	NMR imaging	236
6.4.3.1	Strong field gradients	238
6.4.3.2	Fast imaging methods	239
6.4.3.3	Application to porous materials	239
6.5	Advantages and limitations	240
	References	241
7	Small-angle scattering	247
7.1	Theoretical aspects	248
7.2	Experimental procedure	251
7.2.1	Small-angle X-ray scattering equipment	251
7.2.2	Small-angle neutron scattering equipment	253
7.2.3	Data collection	255
7.3	Plots obtained	259
7.3.1	Guinier plot	261
7.3.2	Porod plot	265
7.4	Range of sizes	268
7.5	Application to cement pastes	269
7.5.1	Guinier plot and radius of gyration	270
7.5.2	Porod plot	271
7.5.3	Scattering contrast	273
7.5.4	Surface area	274
7.5.5	Structure of cement paste	276
7.5.6	Fractal dimensions	276
7.5.7	Factors affecting the results	278
7.6	Advantages and limitations	280
	References	281
8	Microscopic techniques and stereology	286
8.1	Optical microscopy	287
8.1.1	Types of microscopes	288
8.1.2	Characteristics of the microscope	290
8.2	Scanning electron microscopy	291
8.2.1	Design and physical basis of operation	292
8.2.2	The performance and characteristics of the SEM	293

- 8.2.3 Electron-specimen interactions and principal images 294
  - 8.2.3.1 Secondary electrons 296
  - 8.2.3.2 Backscattered electrons 296
- 8.2.4 Environmental scanning electron microscopy 297
- 8.2.5 Transmission electron microscopy 297
- 8.3 Scanning acoustic microscopy 298
- 8.4 Image analysis 299
  - 8.4.1 Image analysis steps 300
    - 8.4.1.1 Preparation 300
    - 8.4.1.2 Detection and measurement 301
    - 8.4.1.3 Digitizing 301
    - 8.4.1.4 Image processing and analysis 301
- 8.5 Stereology 302
  - 8.5.1 Point counting 304
  - 8.5.2 Lineal analysis 306
    - 8.5.2.1 Pore volume 307
    - 8.5.2.2 Pore size distribution 307
  - 8.5.3 Section analysis 308
    - 8.5.3.1 Pore volume 309
    - 8.5.3.2 Pore size distribution from section diameters 310
    - 8.5.3.3 Pore size distribution from section areas 310
  - 8.5.4 Comparison of stereological methods 311
    - 8.5.4.1 Comparison for pore volume 311
    - 8.5.4.2 Comparison for pore size distribution 311
- 8.6 Application of microscopic techniques to cement paste microstructure analysis 312
- 8.7 Air voids analysis using optical microscopy 316
  - 8.7.1 Factors affecting results 316
    - 8.7.1.1 Specimen preparation 316
    - 8.7.1.2 Magnification 317
    - 8.7.1.3 Operator objectivity 317
    - 8.7.1.4 Inclusion of entrapped voids 318
    - 8.7.1.5 Methods of measurement 318
    - 8.7.1.6 Thin sections vs. polished sections 318
  - 8.7.2 Different mathematical parameters 319
  - 8.7.3 Image analysis on air voids 319
  - 8.7.4 Section analysis used to determine air content 321
  - 8.7.5 Air void distribution 323
- 8.8 Advantages and limitations 324
- References 326

9 Comparison of results by various methods	332
9.1 Comparison with MIP results	333
9.1.1 Nitrogen adsorption	333
9.1.2 Helium pycnometry	337
9.1.3 Alcohol exchange and water absorption	339
9.1.4 NMR vs. MIP and nitrogen sorption	341
9.2 Comparison with nitrogen adsorption	342
9.2.1 Water sorption	342
9.2.2 SAXS and SANS	342
9.3 Comparison with replacement techniques	343
9.3.1 Helium pycnometry vs. methanol sorption	343
9.3.2 Alcohol exchange vs. water saturation	344
9.3.3 SANS vs. water absorption	344
9.4 Comparison with microscopy techniques	345
9.4.1 MIP vs. OM	345
9.4.2 MIP vs. SEM	345
References	348
 <i>Summary and conclusions</i>	351
<i>List of related International Standards</i>	359
<i>Glossary</i>	365
<i>Name index</i>	371
<i>Subject index</i>	383